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Influence of environmental relative humidity on the tensile and rotational behaviour of hemp fibres

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Abstract

The aim of this study is to throw new light on the influence of moisture on the mechanical properties of hemp fibres. Indeed, the behaviour of plant-based fibres depends strongly on their humidity. Although this topic has been relatively well treated for the case of wood, the literature on fibre stemming from annual plants is unfortunately poor. This purpose is however of great importance, particularly in view of the production of high performance composites.

The influence of environmental conditions on the static and dynamic tensile moduli, and the strength of elementary fibres are investigated using a versatile experimental set-up. Novel equipment was also designed, to measure the rotation of a fibre about its axis when it was subjected to static loading and moisture variations.

Water sorption is shown to have a significant influence on the apparent tensile stiffness, strength and fracture mode of such fibres, and is also shown to act like an activator of the stiffening phenomena under cyclic loading. A remarkable increase in the fibre stiffness of up to 250%, is measured. Significant longitudinal elongation, reaching a value in excess of 2%, is associated with this increase in stiffness. The absorption and desorption of moisture also leads to substantial rotation of the fibre about its axis.

Water sorption certainly involves a modification of the adhesion between cellulose microfibrils and the amorphous matrix. Under cyclic loading, the cellulose microfibrils could be able to creep into the relaxed amorphous matrix, leading to their re-arrangement, with more parallel orientations with respect to the fibre axis.

Key words: hemp fibres / tensile testing / water sorption / stiffening / damage / DMA

1 Introduction

In recent decades, Organic Matrix Composites, usually made of epoxy and unsaturated polyester, and reinforced with glass or carbon fibres, have played a significant role in the conventional structural materials landscape in various industrial fields. The interest in composite materials is driven by performance as well as environmental factors: the requirement for high strength and stiffness, together with a low specific weight and high corrosion resistance. However, with growing ecological concern and legislative requirements related to material recycling, cellulosic fibres derived from annual plants such as hemp, flax, coir, sisal, and abaca are an interesting alternative to mineral fibres in composite applications, and are particularly competitive with glass fibres. They are cheap, abundant and renewable, and have good specific properties. The current application of plant fibres in composites is that of non-structural components, with random fibre orientations. These components are used by the automotive and building industries. The next step is to attract industrial interest towards the use of plant fibres in load-bearing materials. This use in high performance composite applications requires an accurate understanding of their mechanical behaviour. Unlike classical synthetic fibres, the behaviour of plant-based fibres depends strictly on their humidity. Unfortunately, only a limited number of studies have been conducted on the influence of water on the mechanical behaviour of natural fibres [1-12]. As for wood, it is well known that the moisture content of natural fibres increases with relative humidity, leading to dimensional changes [8-10]. Water, in the form of water vapour or liquid water, penetrates into the fibres. It then breaks the secondary interactions between cellulose macromolecules, and is adsorbed into the cell wall by hydrogen bonds, causing swelling of the fibres [10]. As explained by Pejic *et al.* [10], hemp fibre-water interactions can be explained by competition between hydroxyl groups of the constitutive polymers, and those of the polymer and a water molecule or a water cluster. The sorption kinetics are shown to be dependent on the initial water content [11] and temperature [12] of the plant fibres. At high humidities, absorption and desorption processes are non-Fickian over the full range [11]. From the mechanical point of view, Davies and Bruce [1] have demonstrated a consistent relationship between the elastic modulus and the environmental relative humidity, for flax and nettle fibres. Van Voorn *et al.* [4] demonstrate that relative humidity affects the strength of flax and sisal fibres. Maximum strength occurs at a relative humidity of 70%, and decreases when the RH increases or decreases with respect to this point. According to Stamboulis *et al.* [5], flax fibres maintain an almost constant tensile strength as a function of humidity, with a small increase occurring at a relative humidity of 66% and 93%. However, prolonged exposure may lead to a degradation of their mechanical properties, resulting from the

development of fungus on the fibre surface [5]. Baley *et al.* [3] also revealed that drying significantly influences the tensile strength of flax fibres, and pointed out that irreversible mechanisms are induced when the fibres are dried and then rehumidified. Mannan and Robbany [7] emphasised the existence of hysteresis in the curves of moisture recovery vs relative humidity, and relative length vs relative humidity, and they also highlighted for the first time the influence of humidity on the rotation of jute fibres. Symington *et al.* [2] compared the mechanical properties of seven natural fibres, according to four different conditions of moisture. Using Atomic Force Microscopy on cellulose microfibrils, Lee *et al.* [8-9] recently showed that the time scales for moisture content and dimensional changes are different. They also claimed that changes in moisture content of the microfibrils occur more rapidly than their mechanical relaxation. Astley and Donlad [6] studied the influence of hydration on the distribution of cellulose microfibrils in the S2 layer of flax fibres, using small angle x-ray scattering. A current review of the literature clearly reveals a qualitative relationship between the strength and stiffness of natural fibres, and the environmental relative humidity [1-3,5]. However, the question of the influence of water content on the mechanical behaviour of natural fibres still remains open, in particular for the case of the production of high performance composites. Many questions also remain open, concerning the structure of cellulose and others polymers, and their interactions with water.

The aim of this paper is to quantify the influence of environmental relative humidity on the mechanical properties of elementary hemp fibres, in particular the quasi-static and dynamic tensile moduli, the ultimate strength and strain, and rotational movements relative to the microstructure.

2 Materials and methods

2.1 Plant material

Hemp fibres (*Cannabis sativa* L.) were procured from the LCDCA Company in France. They were delivered in a jumbled state. Bundles of fibres were washed in water for 72h at 30°C, as recommended by Bourmaud *et al.* [13], in order to facilitate the extraction of elementary fibres. Around 300 elementary fibres were isolated. To facilitate and simplify their handling, thin paper with glue was used as mounting tabs.

2.2 Microscopic examination

The isolated single fibres were firstly examined using polarised light microscopy (Nikon Eclipse LV 150), to determine their outer diameters. The average diameter of each fibre was computed by taking ten measurements along its length. The outer diameter was also measured in the rupture area, following the tensile test, by taking one measurement on each

fracture surface. The fibres were also coated on their outer surface with a thin layer of gold, in a Jeol-JFC1100 Sputter Coater, and were then observed with a Jeol 840 Scanning Electron Microscope using the secondary electron imaging. Several images were digitally recorded for each fibre to identify the fracture mode.

2.3 Tensile tests on an elementary fibre

A Dynamic Mechanical Analyser (DMA Bose Electroforce 3230) was used to perform the tensile and harmonic tests. This instrument uses a moving magnet linear motor to apply loads to the sample. This specific experimental set-up is able to perform quasi-static, harmonic and fatigue tests on elementary fibres. The applied force is measured with a 2 N load sensor, with a resolution of approximately 1 mN, and the displacement is measured using a LVDT with a resolution ranging from 0.1 to 1 μm . The typical operating ranges are: 0.01 to 200 Hz for the loading frequency, -70°C to 300°C for the temperature.

2.3.1 Relative Humidity control

The DMA was associated with a relative humidity (RH) generator (HumiSys HF from Instruquest Inc.), to ensure suitable control of the environment around the natural fibres. This RH Generator is designed to inject humidity into the sample chamber by means of a heated transfer line, with a maximum flow rate of 5L/min. The RH is controlled inside the sample chamber using temperature and humidity sensors placed inside the chamber, a few centimetres from the sample. The typical operating range is 5% to 95% (with a maximum temperature of 75°C). The relative humidity is measured using a RH sensor (Vaisala HMT337) with an accuracy, including hysteresis, non-linearity and repeatability, of $\pm 1\% \text{RH}$ on the range 0-90 %RH and for a temperature between 15°C and 25°C . With this setup, since the time scale for moisture content change is particularly short for natural fibres, variations in moisture content associated with a sample's transfer from the conditioning chamber to the tensile machine are avoided. Indeed, various types of inaccuracy can arise due to experimental difficulties in controlling the moisture content of natural fibres, which can affect the overall accuracy and validity of the results.

2.3.2 Quasi-static tensile tests

The tests were carried out at a controlled temperature of approximately 23°C and several values of relative humidity between 10% and 85%. Sixty elementary fibres were tested at a constant crosshead displacement rate of $2 \mu\text{m}\cdot\text{s}^{-1}$, for each RH level. The clamping length was 8 mm. Tensile properties: the apparent Young's modulus, apparent ultimate strength, and failure strain were determined for each fibre. The effective cross-sectional area was calculated from the average diameter in the failure area, assuming the fibre to be perfectly cylindrical. The apparent

Young's modulus was computed from the linear section of the stress-strain curve, and the strain at failure was determined from the crosshead displacement at rupture.

2.3.3 Harmonic tensile tests

Usually, dynamic mechanical testing provides a convenient method for determining the elastic and loss moduli as a function of temperature, frequency or time, or both. The DMA is commonly used to localise the transition regions, by exploiting the rapid change in modulus observed as a function of temperature. This method can also be used to study the degradation or structural rearrangements of a material under given environmental conditions. Under these conditions, the viscoelastic properties are used as an indicator of material microstructure and changes in composition. This technique has already been successfully used to study the hygrothermal degradation of wood [14-15]. In the present study, the mechanical properties are measured *in situ* on the same, unique fibre. This deterministic approach ensures that the measurements are free of the uncertainties, which would otherwise arise from the strong variations in mechanical properties occurring when a set of fibres is used. As a result of the small size of elementary hemp fibres, the DMA tests are particularly delicate, and require many precautions to ensure the relevance of the results.

The individual fibres were submitted to cyclic loading at around 10 to 15% of the average stress at rupture (which involves a peak-to-peak loading amplitude of approximately 50 mN, and a displacement of approximately 15 μm). The clamping length was about 10 mm. Three replicates were used to confirm the results we present here. For each test, the viscoelastic properties of the fibre were measured at regular intervals, as a function of time. The tests were performed at room temperature and varying levels of relative humidity, at a loading frequency of 1Hz.

2.4 Rotation of an elementary fibre

A specific experimental device was designed to study the rotational behaviour of elementary fibres under static tensile loading and RH variations. The fibres were clamped at the top of an environmental chamber, and suspended with a rotor at the bottom (Fig. 1). A contactless angular position sensor (HEDS optical encoder from Avago technologies) was used to measure the rotation of the fibre, when it was subjected to a constant stress and small variations in environmental relative humidity. The stress was applied by means of a mass suspended from the lower part of the clamp. Three samples have been analysed to check the measurement repeatability and confirm the results we present here. The sensor and the RH Generator were connected to a multifunction data acquisition module (NI USB 6221). A routine was developed in the National Instrument's Laboratory Virtual Instrumentation Engineering Workbench (LabVIEW) environment, in order to directly record the variations in whole fibre

rotation as a function of RH. The same RH Generator was used to inject humidity into the sample chamber, with a flow rate of 500 mL/min.

3 Results and discussion

3.1 Influence of humidity on tensile stiffness and strength

Figure 2 and Table 1 provide a summary of the mechanical properties of the hemp fibres, determined from quasi-static tensile tests at four RH levels: approximately 10%, 25%, 50% and 80%, at a temperature close to 23.5°C. Table 1 gives the mean and standard deviation values of tensile properties against relative humidity and Fig. 2 proposes a statistical approach with the representation of the median value, the interquartile range (IQR) and percentiles points of these mechanical properties. The influence of the environmental RH on the tensile properties can be observed. From the set of results corresponding to the apparent Young's modulus, several interesting remarks can be made. An increase in the mean value of the apparent E-modulus of approximately 0.114 GPa/%RH is observed between 10% and 80% of relative humidity. Using the median value, the apparent E-modulus is seen to increase up to a certain point, corresponding to a relative humidity ranging between 50% and 70%, as the humidity exposure is increased, with a slope of approximately 0.105 GPa/%RH. Beyond this point, the increase in E-modulus seems to speed up with a rate of about 0.168 GPa/%RH. This result is only partially in agreement with the data collected by Symington *et al.* [2] for kenaf and jute fibres, since they observed after the upturn in Young's modulus as the humidity exposure increases, and then after this certain point, a distinct decrease. Fig. 2a also shows that the lower bound, symbolised by the 5th percentile points, is independent of the humidity but the upper bound (95th percentile points) increases with increase in humidity. The upturn in apparent Young's modulus as the humidity exposure increases is quite surprising for these natural fibres derived from annual plants, considering the well-known plasticizing effect of water on heterogeneous amorphous phases in materials. Generally speaking, water acts as a plasticizer and affects the stiffness and softening of homogeneous materials. Nevertheless, ligno-cellulosic fibres have an intricate structure and organisation, and are comprised of a mixture of 3 polymers: cellulose, hemicelluloses and lignins [16]. The observed trends in Young's modulus variation as a function of water uptake could be explained at the molecular scale. The rearrangement of matrix molecules, accompanied by the absorption of bounded water, could increase the value of Young's modulus up to a moisture content threshold. Beyond this moisture content threshold, the plasticization of matrix molecules, or more exactly the replacement of hydrogen bonding within the polymer network of the cell wall by bonds between water and amorphous components (hemicelluloses, lignin and para-crystalline cellulose) could enhance the flexibility of the polymer network. Under axial mechanical loading, the cellulose microfibrils, or more

exactly the crystalline cellulose, could be able to creep in the relaxed amorphous components and to realign up about the fibre axis, and then increase the fibre stiffness. This hypothesis seems to be corroborated by the change observed in the stress-strain curves shape when increasing the relative humidity. Fig. 3a shows the typical stress-strain curves, plotted according to tensile tests for elementary hemp fibres. As observed by Duval *et al.* [17], three types of behaviour are observed: (1) truly elastic, (2) elastic including some plastic flow at a low-midway strain level, and (3) elastic with a non-linear region in the first loading stage. The non-linear behaviour revealed by the stress-strain curve (Fig. 3, curve (3)) has been described by several authors as being a characteristic of natural fibres, and is mainly attributed to the reorientation of the cellulose microfibrils about the fibre axis when they are submitted to axial loading [17-23], particularly in the dislocation areas. Some others hypothesis attributed the non-linear behaviour to the shear deformation of non-crystalline region and to the damage of the cell wall, such as the delamination of wall layers. If these three types of behaviour were observed at the four RH levels (Fig. 3b), it is also obvious that the proportion of curves of type 3 strongly increases for the upper RH level (from 40-45% in proportion for 10, 25 and 50% of RH to approximately 75% for 80% of RH), potentially expressing an increase in the realignment of cellulose microfibrils about the fibre axis. According to the initial value of the cellulose MFA (Microfibril Angle) in the main wall layer, it is conceivable to have beyond the moisture content threshold (corresponding to the relaxation of the amorphous components) and under tensile stress two opposed evolution of E-modulus against RH: a decrease for fibres with large MFA (such as early wood tracheids or coir fibres) and an increase for fibres with small MFA (such as bast fibres). The MFA was determined of about 10° using X-rays diffraction on these hemp fibres [24]. For spruce wood, a threshold moisture content of approximately 8% was identified by Obataya *et al.* [25], with a decrease in E-modulus beyond this threshold value. For the testing of hemp fibres, the threshold value is certainly at the equilibrium moisture content, corresponding to an environmental RH of 50-60%.

Geometrical hypotheses can also be formulated. The elementary fibres have a typical cell plant structure, with a lumen and a rounded polygonal shape and the cellulose microfibrils are spirally wound with respect to the fibre axis. In addition to the effect on the fibre stiffness, the MFA is also well-known for its direct influence on dimensional stability. Fibre swelling due to water uptake can change the MFA, and in this way affect the fibre's stiffness. In order to confirm these hypotheses, sophisticated measurement techniques and devices are required, to determine the microstructure and biochemistry of hemp fibres during the various water sorption stages.

As shown in Fig. 2, it is also clear that moisture has a significant influence on the apparent Ultimate Tensile Stress (UTS) of hemp fibres. The UTS for all the environmental conditions simulated in the present study lies in the range of values described in the literature [26]. Drying

of the fibre appears to significantly lower its strength. An increase in UTS up to 50-60% RH (from approximately 410 MPa at 10% to 685 MPa at 50%), and a stabilization or a slight decrease in UTS beyond this threshold are observed. This evolution is particularly apparent when considering the upper bound of the experimental points (95th percentile points, Fig. 2b). This result is in agreement with the study of van Voorn *et al.* [4], in which flax fibres had a maximum strength at 70% RH, with this strength decreasing when the RH was either increased or decreased with respect to this point. The desorption of water could involve the breakage of hydrogen bonds between the amorphous matrix and the crystalline cellulose, and in this way reduce the fibres' strength. In order to correctly describe this characteristic, the classical approach involving the use of Weibull statistics was applied. Indeed, the Weibull law is one of the most suitable and reliable means of describing the failure probability distribution of fibres. According to Weibull statistics, the probability of failure for a fibre of length L, and an applied stress σ , is given by:

$$P_f = 1 - \exp\left(-\frac{L}{L_0}\left(\frac{\sigma}{\sigma_0}\right)^m\right) \quad (1)$$

where m is the Weibull modulus, σ_0 is the characteristic stress and L_0 is the greatest length of fibre containing only one flaw.

For reasons of simplicity, L_0 is often chosen to be unity. In this case, Eq. 1 becomes:

$$P_f = 1 - \exp\left(-L\left(\frac{\sigma}{\sigma_0}\right)^m\right) \quad (2)$$

where L is a dimensionless quantity.

Using Eq.2, after rearrangements, we can write:

$$\ln\left(\ln\left(\frac{1}{1-P}\right)\right) = m \ln(\sigma) - m \ln(\sigma_0) + \ln(L) \quad (3)$$

A straight line with a slope given by the Weibull modulus (m) should thus be found when $\ln(\sigma)$ is plotted as a function of $\ln\left(\ln\left(\frac{1}{1-P}\right)\right)$. Usually, the value of P is estimated using a function known as the probability index.

$$P = \frac{i-0.5}{n} \quad (4)$$

where n is the number of data points and i is the rank of the ith data point.

Although the length of the gauge has no influence on the fibre's strength, it has a major influence on the Weibull modulus. In reality, the number of flaws increases with increasing volume. Silva *et al.* [27] reported for sisal fibres that the Weibull modulus decreased from 4.6 to

3 when the gauge length was increased from 10 mm to 40 mm. For this reason, and in view of the complexity of performing tensile tests on short fibres, a moderate clamping length of 8 mm was chosen for the tests described here. Fig 4a. shows the Weibull distribution plotted for the different RH levels. The Weibull modulus and the characteristic stresses are determined for each value of RH, using a linear regression (Tab. 2). The fibres tested at the upper RH levels exhibit a higher characteristic stress (determined for a probability of failure of 63%), approximately 1.5 times higher than those tested at the lower RH levels. This trend is also respected for higher or lower probabilities of failure, as shown in Fig. 4b. As suggested by SEM fractography (Fig. 5), the fracture mode and mechanisms are effectively affected by moisture, with a ductile fracture at high RH (with some wall pull-out in the outer part of the fibre) and a brittle fracture at low RH. For dry fibres, micro-cracks were observed on the surface and on the section of the fibre following the tensile test, as shown in Fig. 6. These cracks were not observed prior to mechanical loading. Interlaminar cracks were also observed by Thygesen [16] in the fibre wall after loading. These cracks could have a negative effect on the overall fibre strength, due to the lack of stress transfer through the cell wall, and could thus explain the low strength measured at this level of humidity.

The values of Weibull moduli are relatively low but lie in the same range as those determined by Silva *et al.* [27] for sisal fibres ($m = 4.6$ for a gauge length of 10 mm), and by Kompella and Lambros [28] for cotton and wood fibres (respectively 1.77 and 1.26). The influence of RH on the Weibull modulus is not obvious; the values are comprised between 1.46 and 1.79. These low values of Weibull modulus traduce a high dispersion of the defect size in the fibres. The shape of the curve, showing non-linearity makes the linear regression unsuitable for the determination of the Weibull modulus and gives evidence of the existence of several flaw populations particularly for the lower RH levels.

A correlation between UTS and E was revealed many years ago by McLaughlin and Tait [29], for the case of natural fibres extracted from leaves, stems and other miscellaneous sources, with a mean correlation coefficient of 0.69. In Fig. 7, the UTS is plotted as a function of E for our experimental data. A linear regression is used to fit the data.

$$\sigma_f = M.E \quad (5)$$

where σ_f is the UTS (MPa), E is the Young's modulus (GPa), M is the slope and r^2 is the correlation coefficient.

From our experimental measurements, a good degree of correlation is observed, for the RH levels of 10%, 25% and 80% (Tab. 3); the correlation coefficient varies between 0.94 and 0.97 for these three RH levels. The positive correlation between these two mechanical properties reflects the influence of cellulose specifically that of the microfibril angle and the cellulose content, on the apparent tensile properties. An increase in E and UTS is accompanied by a

decrease in MFA and an increase in cellulose content. The large distribution of the experimental points in the UTS-E-modulus plot seems to traduce a large distribution of MFA in each set of fibres. At 50%, the correlation coefficient is slightly lower (0.85); the curve shows clearly two linear parts (from 0 to 30 GPa and from 30 to 50 GPa). The slope of the first part ($M = 34.3$) is of the same order than for others RH levels, the slope of the second one is about three times higher (96.1). This large increase in strength for the stiffest fibres could traduce an improvement of the adhesion forces at the crystalline cellulose/amorphous components interface by hydrogen bonding with water molecules. The lower value of the M-constant at lower and upper RH could confirm the previously proposed hypothesis, i.e. that the mechanical properties under dry or water saturated conditions are governed by the interface between the amorphous matrix and the crystalline cellulose, rather than by the cellulose microfibrils.

As recently pointed out by Virk *et al.* [30,31], the failure strain can be considered as a key criterion for natural fibres since the strain at failure has a lower variability than other tensile properties. Apparent E-modulus and UTS have effectively high-variability, which arises in great part from the difficulty of determining an accurate fibre cross-sectional area, the strain at failure being independent of fibre cross-sectional area. As it is extremely difficult to determine the lumen's cross-sectional area and cell wall thickness experimentally, most authors, including ourselves, consider the full cross-section of the fibre. So, the presence of the lumen and the hygro-expansion of the cell wall are not taken into account in this work. In agreement with these recent works of Virk *et al.* [30,31], our experimental study clearly points out that the strain at failure has a significant lower Coefficient of Variation (0.26 to 0.42) than the apparent E-modulus and UTS (0.6 to 0.86). Considering the mean value (Tab. 1), the strain at failure increases with RH (from 2.34% to 2.67% between 10% and 80% of RH). This conclusion has to be restrained because the evolution of the median value (Fig. 2) shows that this difference is not really statistically significant. However, this apparently constant behaviour, observed using statistical data, could also be the consequence of antagonistic water-dependent mechanisms, such as: (i) relaxation of the fibre, due to plasticization of the amorphous matrix when the relative humidity increases, involving an increase in the strain at failure [32], and (ii) weakening of the fibre cellulose when it is exposed to moisture.

To better quantify the influence of RH on the mechanical properties of elementary hemp fibres, and particularly to ensure that the measurements are free of the uncertainties which arise from the strong variations in mechanical properties occurring when a set of fibres is used, as previously observed, a deterministic approach, with measurements *in situ* on a same, unique fibre was preferred for the next part of this work.

3.2 Water, an activator of the stiffening phenomenon

The aforementioned and assessed reorientation movements of cellulose microfibrils, could also be at the origin of the specific fibre stiffening behaviour, previously observed for hemp [22] or other cellulosic fibres [18,33] when placed under cyclic tensile loading. This hypothesis appears to be confirmed by recent studies, performed using sophisticated techniques such as X-ray scattering [34-37]. A decrease of several degrees in the microfibril angle was observed during the deformation of the fibre. Fig. 8, section I, of the curves (between 40 and 100 mins along the temporal axis), shows the typical stiffening phenomenon observed in these hemp fibres, when submitted to cyclic loading. To avoid any misinterpretation of the results, due to discrepancies in the tensile mechanical properties of the natural fibres, the data is presented using the normalized value of the modulus. It can be clearly seen that the rigidity of the fibre increases until it saturates at a constant value, after a certain number of cycles. The stiffening value of approximately 1.5, measured at ambient temperature and 50% relative humidity, is of the same order of magnitude as the values specified in the studies of Baley [18] on flax fibres, and Silva *et al.* [33] on sisal fibres. A significant decrease in the fibres' damping capacity is also observed, with a decrease by approximately half in loss factor. This phenomenon has previously been shown to be time-dependent, partially reversible, and also influenced by temperature [22,38]. In the present study, we highlight the strong influence of water on this particular characteristic. Contrary to all expectations, in particular to the results of quasi-static tensile tests, a decrease in relative humidity from 50% to 10% leads to an increase in storage modulus of approximately 15%, and a decrease in damping capacity of approximately 30% (Fig. 8, Part II). This outcome is certainly the expression of an additional re-orientation of the cellulose microfibrils about the fibre axis, induced by a mechano-sorptive effect. The desorption of water molecules, at the interface between the amorphous matrix and the crystallite surface, could provide the microfibrils with greater flexibility in terms of their re-arrangement under axial loading. When the fibre is humidified (after a test duration of 150 mins: Fig. 8, Part III), its rigidity decreases rapidly and the damping capacity increases markedly (the normalized value of E' drops to approximately 1.2, and $\tan(\delta)$ reaches a value in excess of 0.18). This behaviour could be the consequence of plasticization of the amorphous polymer. The most unexpected result is observed after approximately ten minutes of re-humidification (corresponding to 160 min of treatment: Fig. 8, Part IV): contrary to all expectations, the tendency is suddenly reversed, and the normalized E' increases until it reaches the remarkable value of 2.5. This activation of the stiffening phenomena under moist conditions certainly involves two principal mechanisms, related to water absorption and desorption:

- plasticization of the amorphous matrix with water. This could explain the variation of E' and $\tan(\delta)$ during stages II and III, during moisture desorption and the first stage of sorption,

- creep and realignment of the crystalline cellulose microfibrils about the fibre axis, due to softening of the matrix (IV).

The measurement of fibre elongation during mechanical testing seems to confirm this hypothesis (Fig. 8d). The fibre's average elongation increases when it is humidified (IV), and can exceed 2.25% when the environmental relative humidity is increased to 90%. This is attributed partially to swelling of the fibre, due to moisture absorption (about 0.2%), and mainly to the creep of cellulose microfibrils in the softened amorphous matrix. Water could break intermolecular linkages between the constitutive components of the cells' walls and create hydrogen bonding, starting with the formation of a monolayer in which one molecule of water is bonded to two accessible hydroxyl groups, and continuing with the formation of a multilayer of progressively increasing thickness. In this way, water provides greater molecular mobility and flexibility to the macromolecular network. Creep movements could therefore occur between macromolecular chains, and the microfibrils could easily slide along the axis of the fibre, when moisture has been absorbed and the fibre is subjected to repeated stress cycles. In agreement with data provided in the literature [8,12], Fig. 8 also emphasizes the fact that water sorption (humidity absorption or drying) is very rapid: no more than a few minutes are required to observe a strong variation in the mechanical properties, following a change in environmental relative humidity.

This mechanical behaviour of an elementary hemp fibre, under tensile cyclic loading and moisture variations, was unexpected and is of a considerable importance in view of the use of natural fibres in high-performance composite applications. A thermo-hydro-mechanical treatment could be applied to natural fibres before their integration into composite materials, thereby increasing or adjusting their mechanical rigidity or damping capacity, according to the foreseen design and/or application. In view of the stiffening potential of approximately 250% using hygromechanical loading, as described in the present study, and considering a mean Young's modulus of approximately 33 GPa for virgin fibre at ambient RH (Tab. 1), high E-modulus fibres (up to 80-90 GPa) could conceivably be obtained after appropriate treatment. This outcome underlines the considerable and significant potential of hemp fibres for composite materials. Appropriately treated hemp fibres could thus be an excellent alternative to glass fibres in composite applications. This particular "accommodation" behaviour observed under cyclic loading could also have a positive impact on the long-term behaviour of organic matrix composites reinforced with natural fibres.

In addition to microfibril stretching, the insertion and resulting linkage with hydrogen bonding of water molecules, between the cell wall components, could also lead to torsion of the cell wall [23,39]. In view of the experimental difficulties in measuring torque during tensile testing of an elementary fibre, the rotational behaviour of fibres under varying moisture

conditions was studied using a specific device (Fig. 1). This experiment was inspired by the study reported by Mannan and Robbany [7].

3.3 Rotational movements induced by water sorption

Fig. 9 provides a graphical plot of rotation about the fibre's axis, as a function of relative humidity. In agreement with the measurements of jute fibres reported by Mannan and Robbany [7], we observed that hemp fibres rotate about the fibre's axis, as a consequence of moisture absorption and desorption. The angle of rotation increases with increasing relative humidity. A rotation of approximately 25° is measured between 10% and 80% RH. When the RH increases, the fibres rotate in a counter-clockwise direction. The direction of this circular motion is reversed when the fibre dries. In hemp fibres, the microfibrillar orientation corresponds to a Z-twist [40]. In view of this helical microfibrillar pattern, we make the hypothesis that moisture adsorption could lead to unwinding of the cellulose microfibrils. More exactly, and in agreement with the model proposed by Mannan and Robbany [7], the intrusion of water into the amorphous matrix in the inter-lamellar layers could induce swelling of the matrix. The fibrils can thus easily slide along the axis of the fibre, which appears to be consistent with the aforementioned hypothesis. The relationship between rotation of the fibre and RH is non-linear, and hysteresis is observed between the sorption and desorption phases. The path between the first and successive cycles is slightly different.

Contrary to the results of Mannan and Robbany [7], an increase in applied stress does not produce an increase in rotational angle, but rather a slight decrease, from 26° to 21° , for a stress increasing from 40 MPa to 615 MPa. This increased stress could lead to an increase in sliding of the microfibrils, and a slight decrease in the spaces available for the absorption of moisture.

4 Conclusion

- (1) This work clearly points out the great interest of using a deterministic approach to study the influence of humidity on the mechanical properties of natural fibres. Effectively, the stochastic approach is particularly intricate because of the uncertainties which arise from the strong variations in mechanical properties occurring when a set of fibres is used.
- (2) Quasi-static tensile tests on approximately 250 isolated elementary fibres have shown that the influence of moisture content on the apparent fibre stiffness, strength and fracture mode is statistically significant. Contrary to all expectations, apparent E and UTS increase with increasing RH up to a certain point, between 50% and 70% RH. Beyond this point, UTS decreases while the increase in E-modulus speeds up.

- (3) Under cyclic loading and moisture adsorption, an unexpected and remarkable increase in fibre stiffness, by as much as 250%, associated with significant longitudinal elongation in excess of 2%, are measured.
- (4) These behaviours are explained by a rearrangement of the matrix molecules, accompanied by the absorption of water. The threshold RH value could correspond to the saturation level of certain hydroxyl groups in the fibre, at the interface between the amorphous matrix and the cellulose microfibrils. Up to this limit, water uptake leads to an improvement of the adhesion forces at the crystalline cellulose/amorphous components interface and by this way in the fibre's mechanical properties. Beyond this limit, water absorption could induce plasticizing of the amorphous matrix due to water adsorption and the creep of cellulose microfibrils in the relaxed amorphous matrix, leading to their re-arrangement, with more parallel orientations with respect to the fibre axis.
- (5) The absorption and desorption of moisture also leads to a substantial rotation of the fibre about its axis. The direction of rotation, which is counter-clockwise when the fibre is humidified, is attributed to the Z-twist microfibrillar orientation of the hemp fibres, and seems to support the possibility of creep of the cellulose microfibrils.

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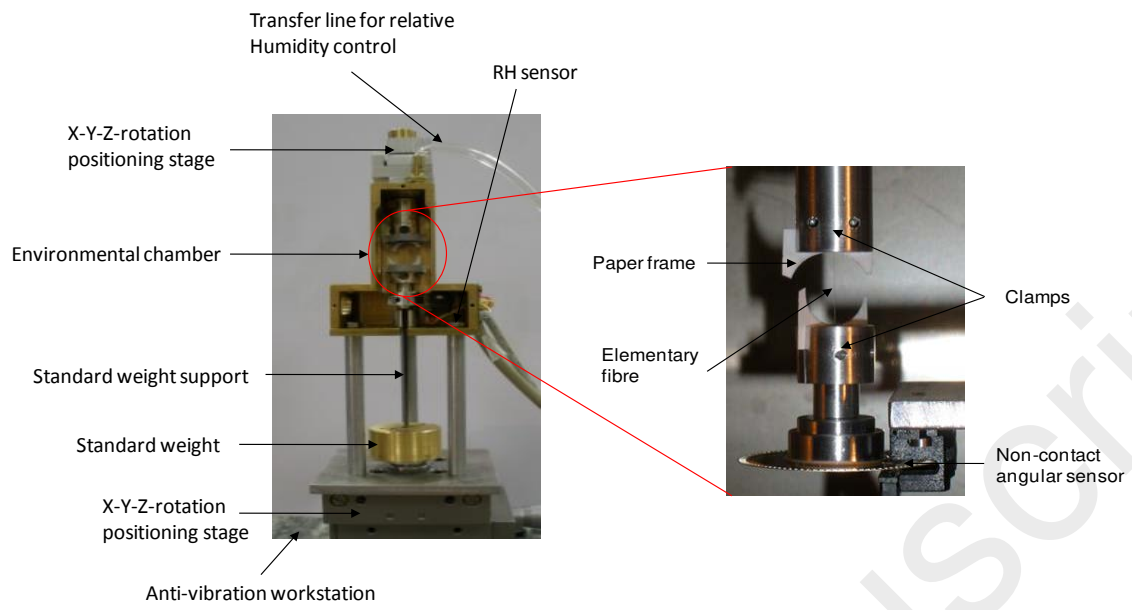


Figure 1: Experimental device for the study of the rotation of cellulosic fibres about their axis, under conditions of static loading and RH variations.

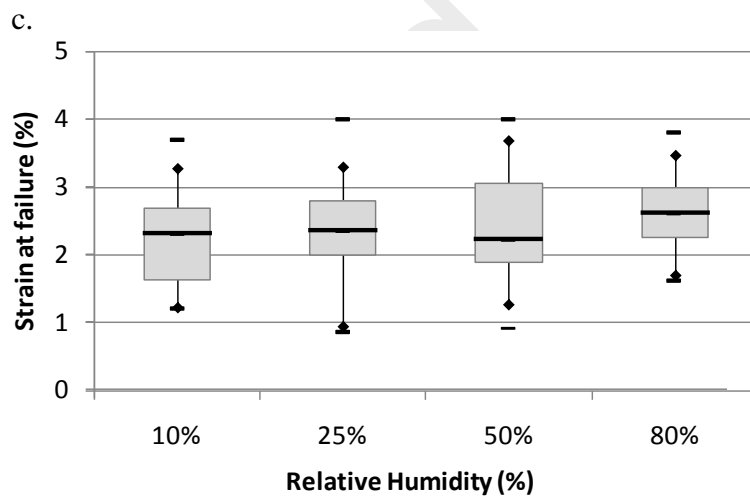
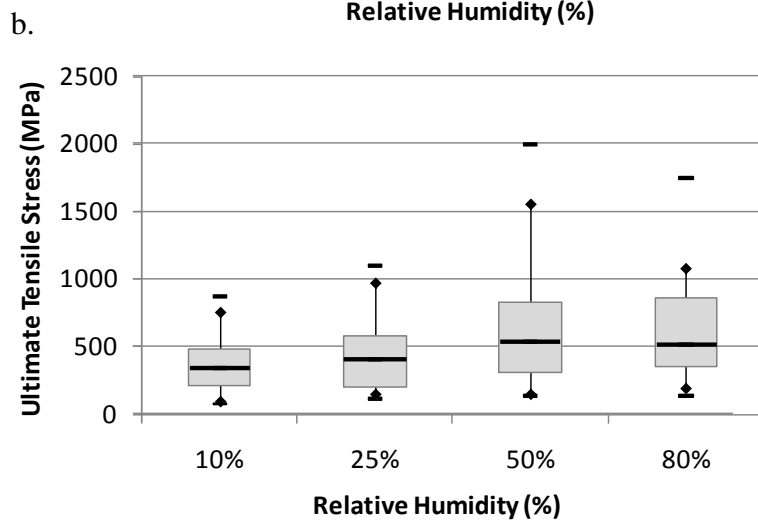
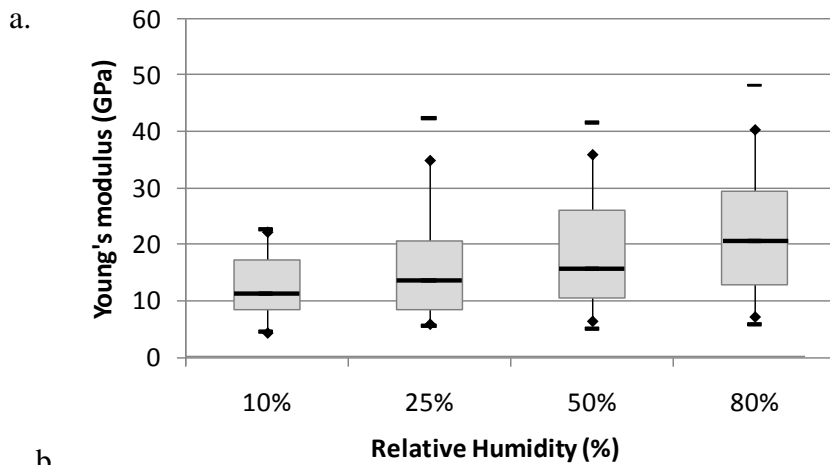
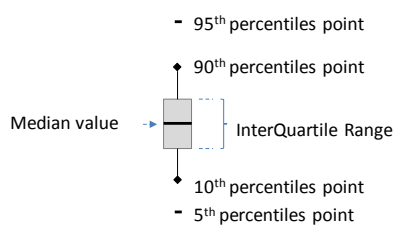
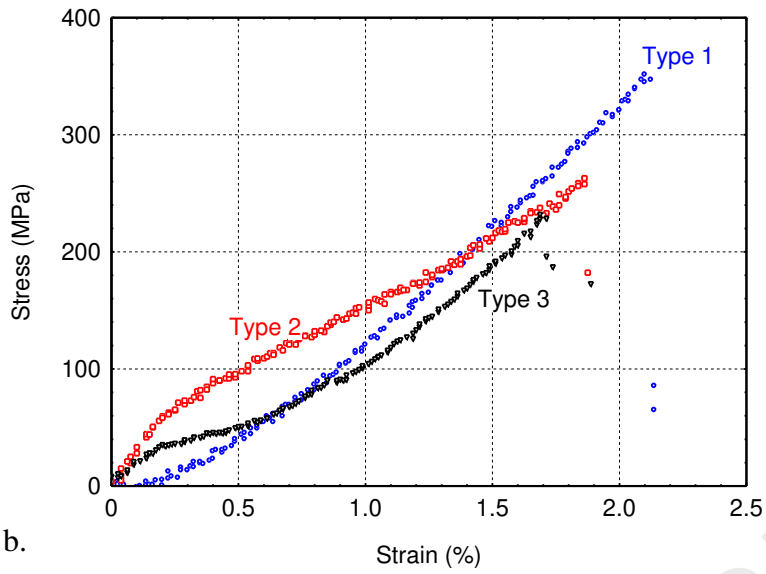


Figure 2: Variations in: (a) apparent Young's modulus, (b) apparent Ultimate Tensile Stress (UTS) and (c) strain at rupture of elementary hemp fibres as a function of the environmental relative humidity.



a.



b.

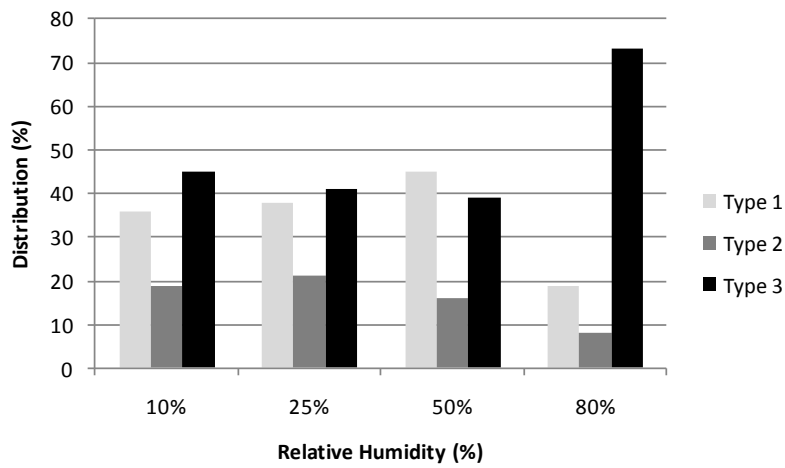


Figure 3: Typical tensile stress-strain curves for elementary hemp fibres (a) and their distribution against relative humidity (b)

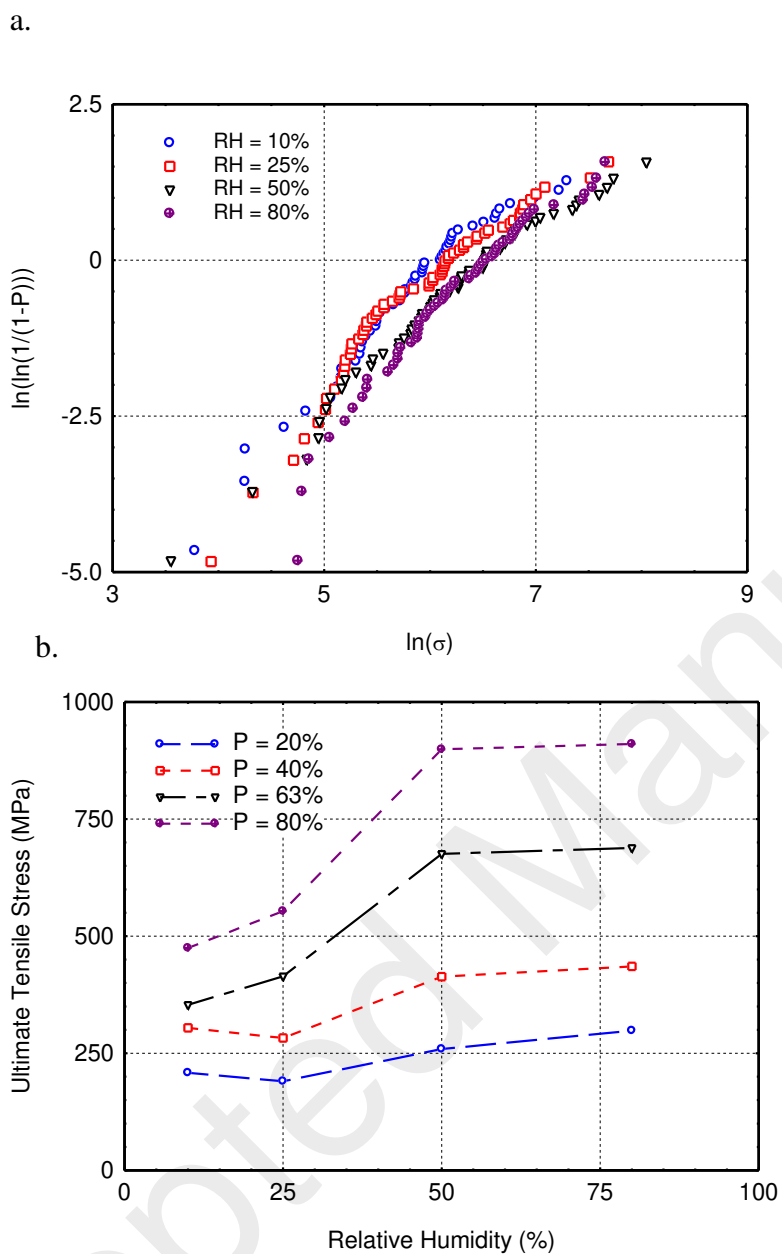


Figure 4. a.Weibull distribution for elementary hemp fibres at four humidity levels. Free length of the fibres: 8 mm. **b.** Apparent UTS against humidity for several probabilities of failure (P : 20%, 40%, 63% and 80%)

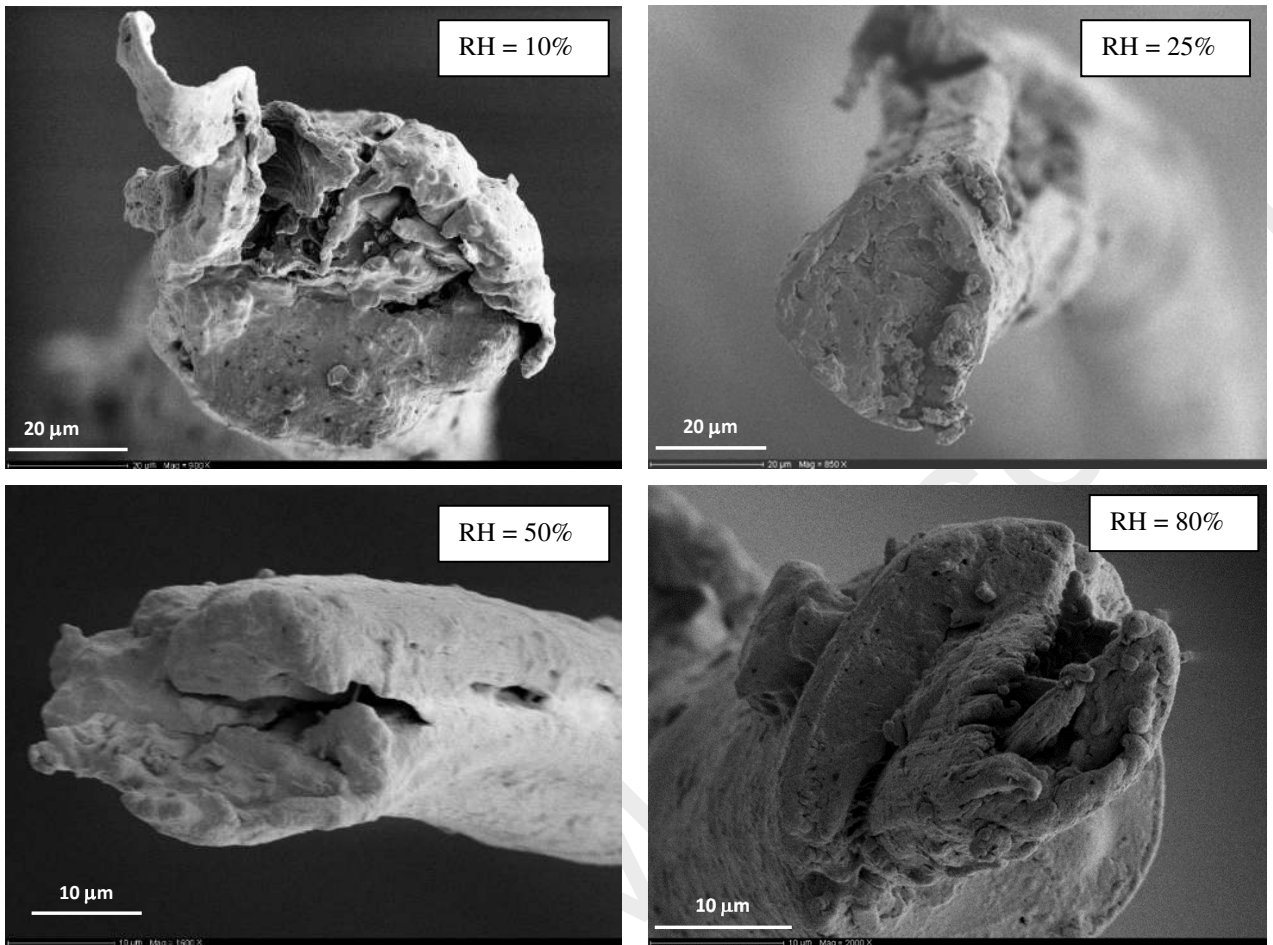


Figure 5: SEM pictures of the fractured surfaces of elementary hemp fibres, following tensile strength tests at different levels of RH.

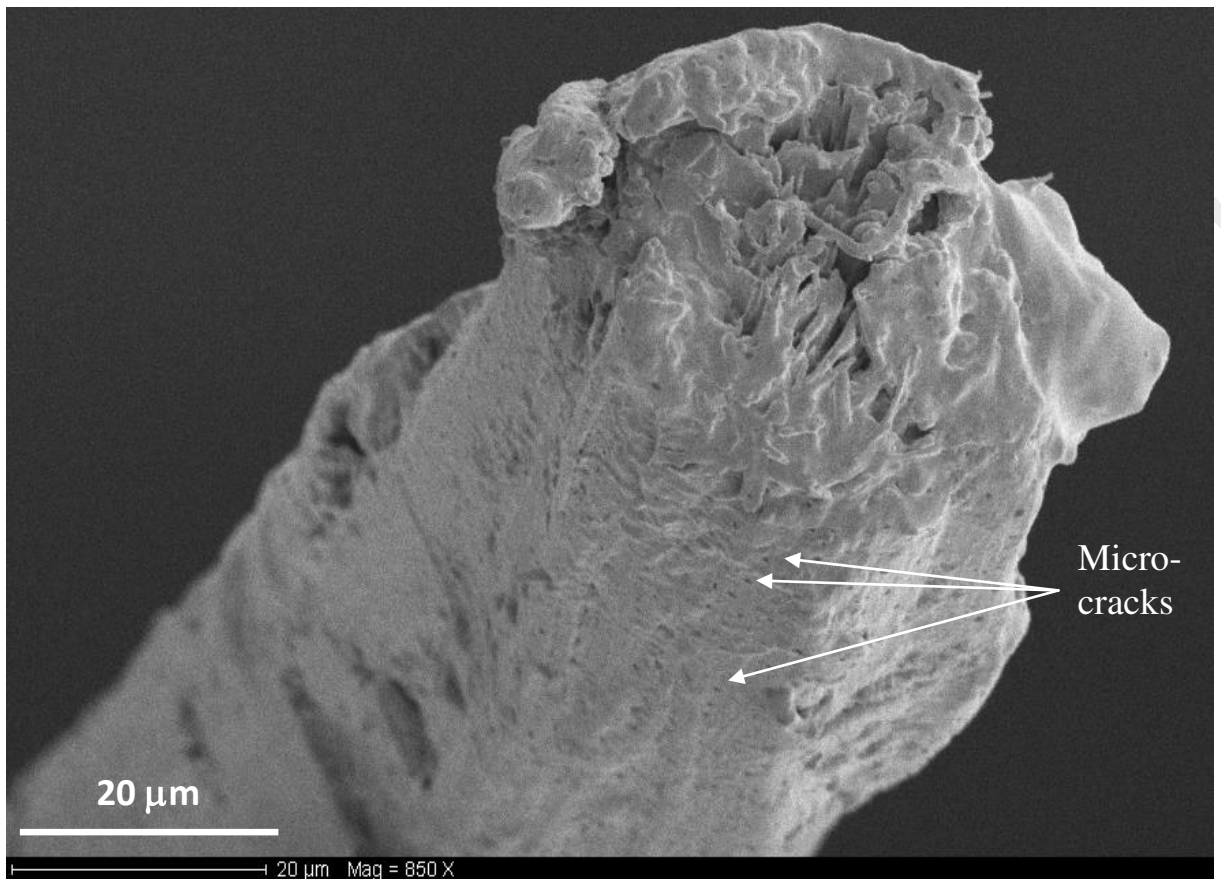


Figure 6: SEM picture of the surface of a hemp fibre, after a tensile strength test at 10% RH. Evidence of micro-cracks inside the cell wall is indicated by the arrows.

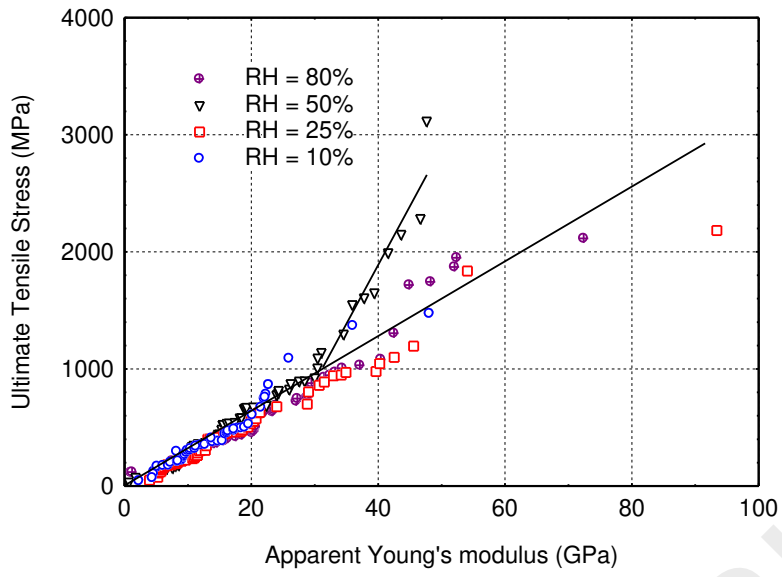


Figure 7: Apparent UTS plotted against apparent Young's modulus, showing a positive correlation.

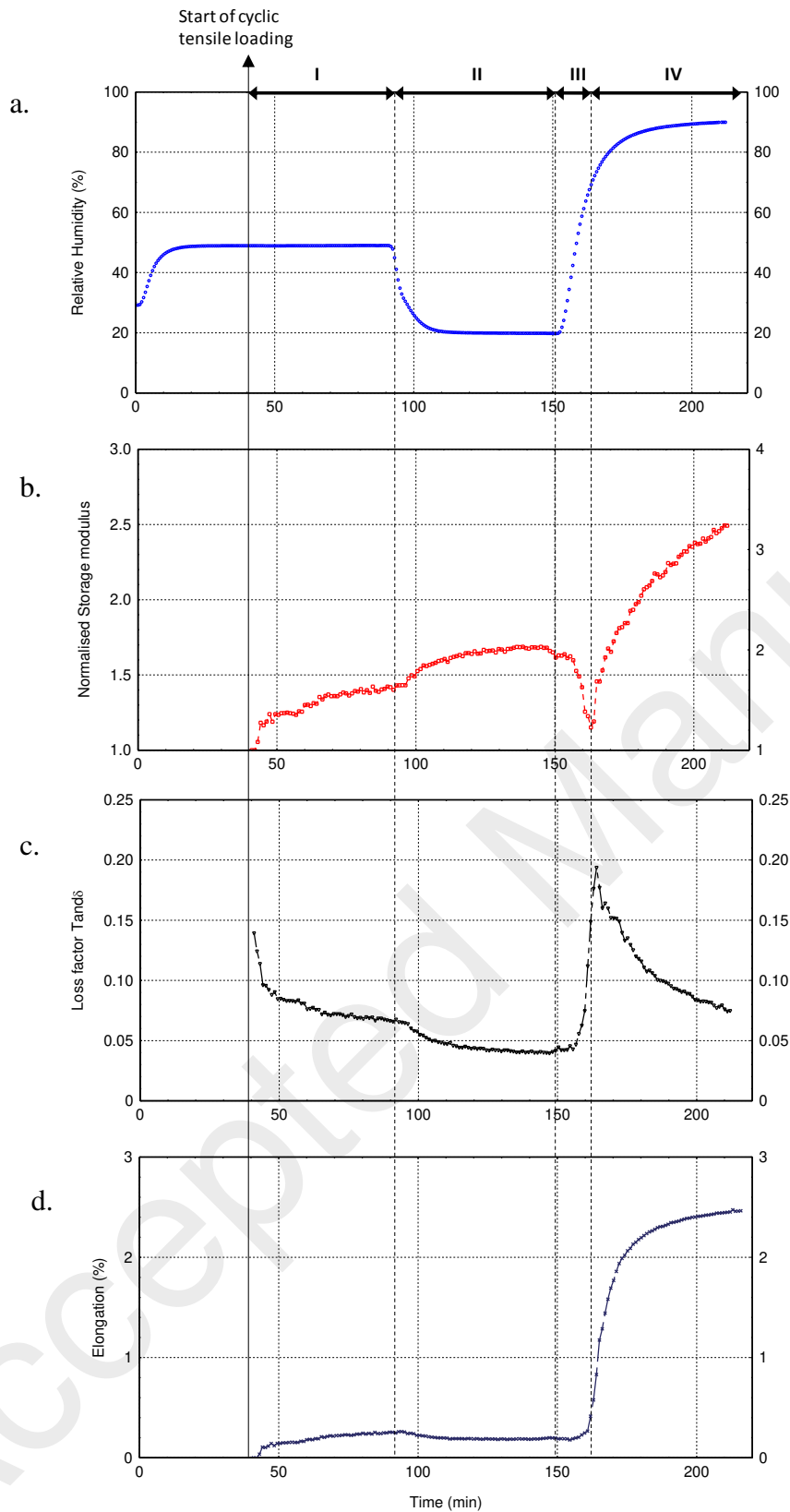


Figure 8: (a) RH, (b) Normalized storage modulus, (c) loss factor, and (d) elongation, as a function of time during absorption and desorption of moisture and tensile cyclic loading. Evidence of the influence of water on the stiffening phenomenon. (Ambient temperature, Loading frequency: 1 Hz)

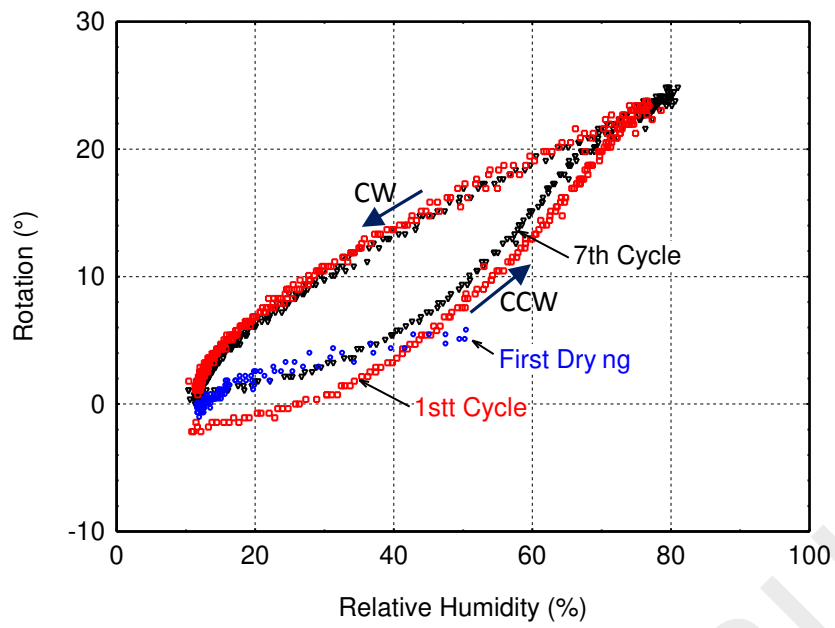


Figure 9: Angles of rotation about the fibre axis vs. percentage of relative humidity, for an elementary hemp fibre at a constant stress of 40 MPa. Direction of circular motion: (+) counter-clockwise (CCW); (-) clockwise (CW).

Relative Humidity (%)	Apparent Young's modulus (GPa)	Apparent Ultimate Tensile Stress (MPa)	Strain at failure (%)	Mean diameter (μm)	Mean diameter close to the rupture zone (μm)
10 (10 \pm 0.7)	13.7 \pm8.2 (2.3...48.1)	408 \pm296 (44...1473)	2.34 \pm0.84 (1.14...5.27)	28.1 \pm6.2 (19.3...42.5)	27.1 \pm7.6 (14.7...41.4)
25 (25 \pm 1.5)	18.3 \pm14.9 (3.9...93.4)	485 \pm399 (51...2182)	2.35 \pm0.84 (0.61...4.2)	24.6 \pm5.3 (13.9...34.5)	24.4 \pm7 (12.6...41.5)
50 (50 \pm 1.1)	19.1 \pm11.3 (1...47.7)	685 \pm590 (35...3118)	2.5 \pm1.06 (0.73...6.94)	25.4 \pm6 (15.9...41)	23.9 \pm7.6 (10.6...45.3)
80 (79 \pm 0.97)	22.7 \pm13.5 (1...72.4)	652 \pm459 (116...2114)	2.67 \pm0.7 (1.26...4.74)	24.7 \pm4.1 (16.5...33.8)	25.4 \pm7.4 (14.4...44.4)

Table 1: Mechanical properties of elementary hemp fibres as a function of RH (Temperature = 23.5 \pm 1.5°C). Mean value \pm Standard deviation (min value...max value)

Relative Humidity (%)	Characteristic stress σ_0 (MPa)	Weibull modulus	r^2
10	450	1.71	0.96
25	470	1.61	0.94
50	673	1.46	0.97
80	680	1.79	0.95

Table 2: Characteristic stress and Weibull modulus as a function of the environmental relative humidity

Relative Humidity (%)	Regression range E (GPa)	M	r^2
10	0 - 100	31.2	0.94
25	0 - 100	26.5	0.97
50	0 - 100	39.5	0.85
	0 - 30	34.3	0.98
	30 - 100	96.1	0.92
80	0 - 100	29.8	0.94

Table 3: Correlation between the apparent Ultimate Tensile Stress and Young's modulus. Parameters of the regression equation for different levels of RH.

Stress (MPa)	Rotation ($^\circ$)
40	26
155	23.5
270	22.3
615	21

Table 4: Angles of rotation of a hemp fibre about its axis, during absorption and desorption of moisture at different stress levels.